

Some electrical properties of sodium silicate glasses modified with titania

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A number of glass samples were prepared from mixtures of SiO_2 , TiO_2 and Na_2CO_3 (for Na_2O) and their electrical characteristics were measured and interpreted in terms of an electrical energy gap somewhat smaller than the optical gaps previously reported for these glasses. Capacitance measurements showed that one effect of increasing the TiO_2 content was to increase the permittivity. Traditional sodium silicate glasses conduct electricity by ions, but the admixture of TiO_2 brings a significant electronic contribution. Some measurements at high electric fields were made and evidence of the applicability of small polaron theory to the results is presented.

1. Introduction

Many papers have appeared in recent years reporting the properties of amorphous and glassy semiconductors and much of the state of the art is included in a book written by Mott and Davis [1]. It is clear that even with materials devoid of long-range order and with band-tailing beyond the normal conduction and valency bands, a forbidden gap exists and may be estimated from measurements of electrical conductivity at low applied fields, as a function of temperature. Mott [2] and Cohen [3] regard the gap measured, assuming the measured energy gap to simulate that of an intrinsic semiconductor, to represent the energy difference between mobility edges. Other authors have suggested that the energies derived from measurements of electrical conductivity with temperature represent the energies needed to excite electrons between trapping centres. Davis and Mott [4] modified the original Cohen-Fritzsche-Ovshinsky model to postulate a peak in the density of states curves near the middle of the gap. Such states could arise from dangling bonds and are more readily postulated for amorphous and/or covalently-bonded materials than for glasses and/or ionically-bonded materials.

In the present work we have tried to investigate how the simple electrical properties of our glasses depend on composition and to what extent the

properties are analogous to the much more widely examined chalcogenide glasses.

One similarity between our glasses and the chalcogenides has already been reported. This is the observation of memory switching [5]. Other similarities lie in the form of optical absorption edges associated with forbidden non-direct transitions [6].

2. Experimental procedures

2.1. Material preparation

High purity TiO_2 , SiO_2 and Na_2CO_3 (as a source of Na_2O) were the starting materials. The glasses were made in 20 g melts in a 25 ml platinum crucible. The melts were stirred and the furnace temperature increased to 1300°C in about 6 h. By slow heating it was hoped to reduce mechanical and volatilization losses. The compositions of the melts are given in Table I expressed in wt%. The following observations were made.

(1) Some glasses developed a hazy appearance which increased with increasing SiO_2 content.

(2) All the ternary glasses containing 5 to 15% TiO_2 were colourless, except when viewed edge-wise.

(3) As the ratio of Na_2O to SiO_2 is increased, the amount of coloration of the glasses decreases rapidly, so that glasses are prepared whose colours

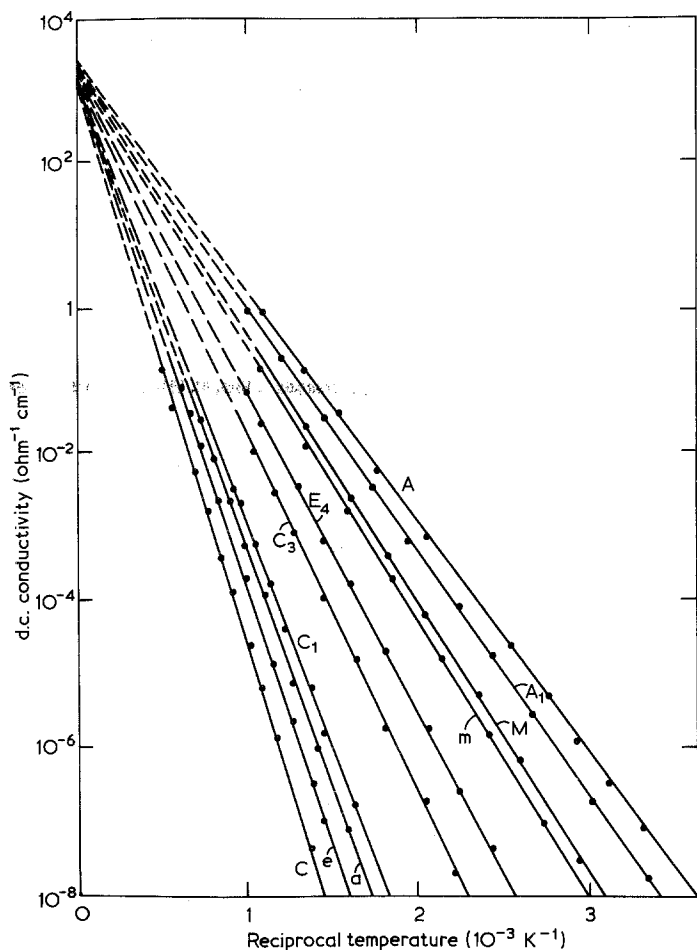


Figure 1 Electrical conductivity as a function of reciprocal temperature for ten glass specimens.

compare favourably with PbO glasses having comparable optical properties.

(4) Due to their hygroscopic nature, none of the binary glasses could be polished in a water medium.

After fining, the glass was poured on to a graphite block and cooled. It was then crushed and re-melted in an effort to ensure homogeneity. After the second melting the glass was poured and the samples were cast and transferred to the annealing furnace and heated to 600°C before being allowed to cool gradually to room temperature over a period of about 4 h.

2.2. Electrical measurements

Disc-shaped samples were made by casting and polishing and electrodes of aluminium were evaporated to form a guard-ring and then central electrodes of gold were evaporated on. The samples had thicknesses in the range 1 to 2.5 mm. A stabilized power supply was used to provide a voltage source and the circulating currents were

measured with the aid of a Keithley electrometer. All measurements were carried out in a vacuum system at a pressure of 10^{-5} to 10^{-6} torr. The temperature of the samples could be monitored using a chromel-alumel thermocouple attached to the top electrode and a Comark electronic thermometer.

3. Experimental results

3.1. Low-field conductivity

Fig. 1 shows the results of measurements of $\log \sigma$ against reciprocal temperature (σ being the d.c. conductivity.) These measurements were made in the low applied voltage range in which the conduction was ohmic in character. They show a series of straight lines which all intersect the $\log \sigma$ axis in the region $\sigma \approx 10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$. At first appearance these curves are of the kind normally associated with intrinsic semiconduction. If this is indeed the case then a value of twice the activation energy for each curve should give a value for an electrical energy or mobility gap [1].

TABLE I Some properties of ternary Na₂O–TiO₂–SiO₂ glasses

Melt. No.	Na ₂ O content (wt %)	SiO ₂ content (wt %)	TiO ₂ content (wt %)	Relative density	Optical gap E_{opt} (eV)	Electrical gap E_{el} (eV)	$\sigma_0 \times 10^3$ ($\Omega^{-1} \text{cm}^{-1}$)	Dielectric constant
E_0	23.65	68.73	7.62	2.71 ₍₂₎	2.94	0.85	4.1	7.0
E_1	30.67	59.44	9.88	2.73 ₍₀₎	2.65	0.86	4.3	9.5
E_2	27.92	54.09	17.99	2.74 ₍₂₎	2.20	1.16	5.5	10.0
E_3	25.61	49.63	24.76	2.78 ₍₈₎	2.74	1.17	2.14	
E_4	23.66	45.85	30.89	2.79 ₍₃₎	2.30	1.36	3.20	11.5
E_5	25.00	40.00	35.00	2.80 ₍₇₎	2.28	1.35	2.30	
E_6	20.53	39.69	39.78	2.83 ₍₉₎	2.90	1.33	2.40	12.0
A_1	21.97	63.87	14.16	2.71 ₍₂₎	2.48	0.86	2.30	9.7
A_2	20.51	59.64	19.84	2.73 ₍₅₎	2.52	0.87	1.69	9.7
A_3	17.12	49.77	33.11	2.82 ₍₄₎	2.64	1.62	1.90	12.4
C_1	18.12	70.21	11.67	2.69 ₍₇₎	2.28	0.83	2.10	9.7
C_2	17.12	66.34	16.54	2.70 ₍₀₎	2.58	0.86		9.7
C_3	16.22	62.87	20.91	2.72 ₍₀₎	2.84	1.10	1.80	9.8
C_4	15.42	59.64	24.88	2.73 ₍₉₎	2.80			
C_5	25.61	49.63	(24.76	2.78 ₍₆₎				
C_6	25.61	49.63	(+1% Cu ₂ O (24.76	2.80 ₍₆₎		2.70	1.89	
M_1	25.00	60.00	15.00	2.72 ₍₂₎	2.47	1.49	4.00	6.6
M_2	25.00	55.00	20.00	2.74 ₍₅₎	2.54	1.22	2.30	8.1
M_3	25.00	50.00	25.00	2.79 ₍₀₎	2.66	1.06	2.80	10.0
M_4	25.00	40.00	35.00	2.80 ₍₇₎	2.86	1.31	2.45	12.6
M_5	25.00	35.00	40.00	2.90 ₍₅₎	2.76	1.33	2.50	14.3

Thus initially we have analysed the results using an equation of the form

$$\sigma = \sigma_0 \exp(-E_{\text{el}}/2kT)$$

The extrapolated conductivity σ_0 is a constant and is related to the effective density of states and to the carrier mobility. E_{el} is the derived energy gap. Table I lists the derived values of E_{el} and relates them to composition and to the values of optical energy gap previously reported.

3.2. Effects at higher electric fields

Although the current at low applied fields is essentially ohmic it shows higher current levels when an electrical field greater than about $2 \times 10^3 \text{V cm}^{-1}$ is applied, and this behaviour is observed at elevated temperatures as shown in Fig. 2. Similar modes of behaviour were observed for glasses of other compositions.

3.3. Time dependence of direct currents

The time dependence of current at an applied voltage of 200 V was studied for periods up to 24 h for specimens of different composition and held at temperatures of 300° C as well as room temperature. As a general rule the current remained constant over these extended periods suggesting the current to be electronic rather than ionic in

our glasses. With some glasses at room temperature there was an absorption current during the initial few seconds for which the field was applied and this probably arose as a result of retarded polarization due to titanium ion migration. This would predominate over that of the monovalent and larger sodium ion because of its higher charge and small ionic radius, combined with its high coordination number.

3.4. Film thickness and electrode effects

For our ordinary measurements of current–voltage characteristics of normal specimens having different thicknesses, the results confirm the absence of non-linear potential falls across the samples. No dependence of the current for a given applied voltage was found for a number of similar glass samples carrying electrodes of different materials (gold, silver, copper and aluminium.)

3.5. Measurements under alternating fields

The dielectric properties of TiO₂ have been extensively investigated and in the present measurements we used simple capacitance techniques to study the permittivity of the glasses in the low-frequency range 60 Hz to 30 kHz at room temperature. In particular the effects of adding TiO₂ were studied with the general result that the addition of TiO₂

led to an increase in the permittivity of the glass as shown in Table I.

4. Discussion

So far as the general question of glass formation is concerned the role of titania is rather important. The density of the glasses increases as the titania content is increased. Within the extremes of composition shown in Table I (15–30% Na₂O; 70–35% SiO₂; 10–40% TiO₂; admixtures up to 5% Cu₂O,) usable optical glasses of relatively low density may be obtained. The optical absorption data seem appropriately explained on the basis of a model involving forbidden indirect electronic transitions [6] and a reasonable optical energy gap. However the electrical conduction measurements lead to some difficulties of interpretation. Glasses containing significant proportions of sodium are generally thought to be ionic conductors but the order-of-magnitude agreement of the optical energy gap and the electrical gap calculated on the assumption that the samples behave as intrinsic semiconductors, suggests that the addition of titanium has modified the normal conduction mechanism in alkali glasses and indeed the effect of titanium is to make electronic conduction a more important process than ionic conduction. The absence of a time dependence of current with applied voltage supports this view.

This conclusion agrees with the derived ideas from previous work on oxide glasses containing titania. Turnbull and Lawrence [7] in their interpretation of molar refraction measurements showed that titanium in glass maintains a co-ordination number of 6. Other studies of the system have shown that the high charge and small radius of the Ti⁴⁺ ion results in a high local field strength and this reinforces the glass network and also raises the dielectric constant [8] and lowers the electrical conductivity of specimens, as shown from the data in the Table. Hirayama and Berg [9] showed that in glasses containing comparable quantities of titanium and sodium the effect of the former ion would be greater than that of the latter.

Since titanium is a member of the same group of 3d elements as nickel and since the Hall mobility [10] in TiO₂ has a value similar to that in NiO $\sim 0.2 \text{ cm}^2 \text{ V}^{-1} \text{ Sec}^{-1}$ at 300 K, and its temperature dependence is the same, the choice of TiO₂ for the search and study of polaron conductivity mechanism is rather interesting as com-

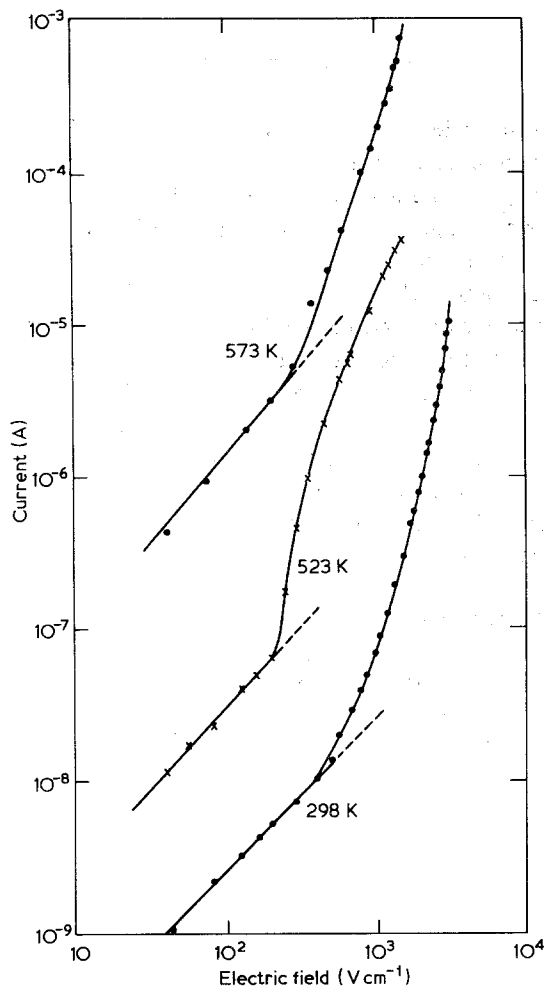


Figure 2 Current as a function of applied electric field for a sodium-titanium-silicate glass (17.99% TiO₂; 27.92% Na₂O; 54.09% SiO₂) at three temperatures.

pared to NiO. A detailed study carried out by Bogomolov *et al.* [11] has given strong evidence for conduction by small polarons in rutile and the polarization phenomena would be expected to be similar when the titania is dispersed in the glass but maintaining its Ti⁴⁺ ionic form.

This interpretation is sustained by the recent experimental work by Sayer and Mansingh [12]. They conclude that for semiconducting phosphate glasses based on oxides of Ti, V, Mn, Fe, Co, Ni, Mo and W a polaronic model is shown to be generally applicable. The variation of activation energy for conduction with type of glass and the transition metal ion (TMI) spacing is found to dominate the magnitude of the conductivity.

An analysis of the curve of current as a function of electric field given in Fig. 2 particularly at the higher fields shows the conductivity to vary as

$$\sigma(E) = \sigma(0) \frac{\sinh(eaE/2kT)}{eaE/2kT}$$

as expected for a simple hopping model [13] where $\sigma(0)$ is a constant, E is the electric field and the jump parameter a , the average distance a carrier hops, is appreciably larger than the ion spacing. From the equation the sinh term implies non-ohmic behaviour when $eaE \simeq kT$ and an increase in mobility for $a = 15 \text{ \AA}$ and $T = 298 \text{ K}$.

However, the large values of a could be due to localized carriers at impurity sites [14] and any local ordering could also effect these values. Therefore in our glasses containing TiO_2 , the polaron conductivity mechanism may be associated with the high field slopes and the small polaron theory seems to be applicable.

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